8. Project Report to Defra

This project is a direct extension of the contract RMP2258 “Acid Deposition Processes” which ended on 31 October 2006 (see Final Report to Defra, February 2007), and as such follows the format and objectives established for that contract. The overall programme of work was divided into 11 work packages, and the work in the extension followed the original contract, but was regrouped into 4 work packages. The objectives of the extension (from the SID3 form) were linked to the work packages in the research plan, and were:

a) Continue the measurements of dry deposition of SO₂ and NH₃ over representative terrestrial surfaces in the UK, and cloud composition, to maintain the long-term datasets that currently exist.
b) Develop and improve the methods for estimating both dry and wet deposition of acidifying and eutrophying substances, in order to improve the theoretical basis of these estimates, and to validate them by direct measurement.
c) Measure the dry deposition rates of atmospheric aerosol to improve parameterization of particle deposition in models.

[Note: this objective was modified to accommodate objective (i) below, August 2008]
d) Produce high resolution (1km x 1km) maps of annual wet and dry deposition throughout the UK, and a measure of the uncertainty associated with such maps, specifically for years 2004 and 2005 (dry deposition); 2005 and 2006 (wet deposition and cloud).
e) Produce maps of the UK showing annual ozone AOT 40 at 1 km x 1 km, and a measure of the uncertainty associated with such maps, specifically for 2006 and 2007.
f) Synthesise the results from the project, and other information, to provide well-founded strategies for advising policy decisions.
g) Provide support for the work of Rota in analysing, interpreting and synthesizing data.
h) Maintain and improve the delivery of data for DEFRA and its stakeholders, through written reports, peer-reviewed papers and a regularly updated website.
i) Operate aerosol analyzers as part of September 2008 EMEP ‘Intensive’ field campaign at Bush and Harwell.

1. CONTINUE THE MEASUREMENTS OF DRY DEPOSITION OF SO₂ AND NH₃ OVER REPRESENTATIVE TERRESTRIAL SURFACES IN THE UK, AND CLOUD COMPOSITION (OBJECTIVE A).

1.1 Dry deposition of SO₂: Continuous fluxes at Auchencorth and Sutton Bonington, 2007

The dry deposition of SO₂ has been monitored continuously at Auchencorth and Sutton Bonington since 1995 and is ongoing to date. The data from 2007 are reported here although the analysis for Sutton Bonington is provisional at present. Table 1.1 below gives the data capture obtained at each site. The data capture for SO₂ at Auchencorth is quite small as concentrations are now below the detection limit of the analyser for much of the time. A new analyser was installed in January 2008 which should be able to resolve lower concentrations.
Table 1.1: Data capture achieved at Auchencorth and Sutton Bonington in 2007

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Auchencorth Moss</th>
<th>Sutton Bonington</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Raw %DC</td>
<td>Filtered %DC</td>
</tr>
<tr>
<td><strong>SO₂ concentration gradient</strong></td>
<td>99%</td>
<td>58%</td>
</tr>
<tr>
<td><strong>Basic meteorology</strong></td>
<td>96-100%</td>
<td>96-100% (with gap filling)</td>
</tr>
<tr>
<td><strong>Turbulence</strong></td>
<td>84%</td>
<td>53%</td>
</tr>
</tbody>
</table>

The pronounced decrease in median concentrations at Sutton Bonington since 1995 has now slowed and there has been little change between 2006 and 2007 (Figure 1.1a). Due to the co-deposition of NH₃ and SO₂ the deposition velocity for SO₂ has increased slightly at Auchencorth (Figure 1.1b) and it is expected that a similar trend will be observed at Sutton Bonington once the data are fully analysed.

![Figure 1.1a: Annual median SO₂ concentration at Sutton Bonington](image)

![Figure 1.1b: Annual median deposition velocity for SO₂ at Auchencorth Moss](image)
1.2 \textit{NH}_3\textit{ flux measurements}

Intensive NH$_3$ flux measurements were made during key management periods over two contrasting grasslands, during a total of three periods:

II. Keenley Fell extensively managed upland grassland, including de-stocking: 18 May – 19 June 2008.

Between period I and II, the AMANDA gradient analyser used for this work underwent a major upgrade which has led to a much more robust operation in the latter campaigns.

1.2.1 NH$_3$ Fluxes over Intensive Agricultural Grassland

Measurements of ammonia exchange were made with the AMANDA gradient analyser at the managed agricultural grassland site at Easter Bush with three objectives: (a) to quantify NH$_3$ exchange during key management periods over intensively managed grassland (following fertiliser application and during animal grazing), (b) to provide a reference measurement for the TAG / TIREA development and (c) as a contribution to the NH$_3$ inter-comparison campaign described in Section 1.2.3 below.

Figure 1.2a shows the time-series of the surface / atmosphere exchange measured at Easter Bush during period I. In 2007, applications of mineral fertiliser were made on 14 March (69 kg N ha$^{-1}$), 16 May (52 kg N ha$^{-1}$) and 11 July (52 kg N ha$^{-1}$). The two latter applications captured with the measurements only led to small emissions of up to 250 ng m$^{-2}$ s$^{-1}$, which were smaller, but significantly non-zero, at night. This confirms that (at least initially) the source is direct emission from fertiliser pellets and soils, which is not under stomatal control and therefore continued during night-time. These fluxes following fertilisation were extremely small compared with previous measurements of fertiliser emissions. This was confirmed by simultaneous flux measurements with QCL absorption spectrometer by the University of Manchester and was likely linked to the large amounts of precipitation preceding and following the applications. By contrast, during some grazing periods (e.g. 17-22 June & 4-12 Aug. 2007), fluxes followed a clear diurnal cycle with emission of up to 400 ng m$^{-2}$ s$^{-1}$ during the day and very small deposition at night. Also some grazing periods include periods of night-time emissions indicating that not all emission originates from the stomata, but directly from the soil. Figure 1.2b shows average daily fluxes in mg NH$_3$ m$^{-2}$ day$^{-1}$ (for comparison, 1 mg NH$_3$ m$^{-2}$ day$^{-1}$ is equivalent to 11.6 ng NH$_3$ m$^{-2}$ s$^{-1}$ or 3.0 kg N ha$^{-1}$ yr$^{-1}$), which are broken down into average daytime and average night-time fluxes. Emissions during this period averaged a substantial 3.6 mg m$^{-2}$ day$^{-1}$ (i.e. equivalent to 11 kg N ha$^{-1}$ yr$^{-1}$), dominated by grazing emissions, which were larger during this period than fertiliser evaporation, due to the meteorological conditions that dominated the different periods.
Figure 1.2a. Time series of concentrations and fluxes of ammonia during the 2007 measurement period at Easter Bush in relation to meteorological parameters.
Figure 1.2b. (upper) Average daily NH$_3$ fluxes measured at Easter Bush over the period 10 May – 15 August 2007. (lower) Split of these average fluxes in average daytime and average night-time fluxes in relation to data coverage for each day achieved with the AMANDA instrument.

The time series of measurement period III, also at Easter Bush, is shown in Figure 1.2c. Much better data capture was achieved with the upgraded AMANDA system. In 2008, mineral fertiliser applications occurred on 4 April (69 kg N ha$^{-1}$), 13 May (52 kg N ha$^{-1}$), 18 June (52 kg N ha$^{-1}$) and 29 July (52 kg N ha$^{-1}$). Urea at 35 kg N ha$^{-1}$ was applied on 28 August during this measurement period, immediately resulting in large emissions of up to 4000 ng m$^{-2}$ s$^{-1}$, which relatively quickly decreased with the rain events on 30 August and 1 September. Prior to fertilisation, fluxes again peaked at about 400 ng m$^{-2}$ s$^{-1}$ and were in the range of the grazing fluxes measured in 2007. Five days after fertilisation, daily fluxes were back in the range of fluxes prior to fertilisation (Fig. 1.2d).
Figure 1.2c. Time series of concentrations and fluxes of ammonia during the 2008 measurement period at Easter Bush in relation to meteorological parameters. The graph shows data that have passed all filter criteria (solid lines) and those that are considered less reliable (dotted lines).
1.2.2 NH₃ FLUXES OVER UPLAND EXTENSIVE GRASSLAND

Although species-rich upland meadows are extremely sensitive to nitrogen deposition there is almost no measurement based information on the parameterisations of NH₃ dry deposition to this type of ecosystem and thus the dry deposition input of N is very uncertain. Thus measurement period II was conducted at an upland grassland which is managed for species richness, with limited grazing and limited fertiliser inputs. For this purpose the infrastructure of the O₃ fumigation experiment at Keenley Fell near Hexham was used and NH₃ gradient measurements were made with the upgraded AMANDA system from 28 May to 19 June 2008. While the field was initially used for grazing at a density of about 6.5 sheep & lamb ha⁻¹, the site was de-stocked on 2 June, in accordance with management regulations for this type of species-rich upland meadow. The measured time series is shown in Figure 1.2e, with daily average fluxes presented in Figure 1.2f.
Figure 1.2e. Time series of concentrations and fluxes of ammonia during the 2008 measurement period at Keenley Fell in relation to meteorological parameters. The graph shows data that have passed all filter criteria (solid lines) and those that are considered less reliable (dotted lines).

The field acted as a clear net source initially, but progressively changed to a net sink after the animals had been removed. This change in flux is mirrored in a decrease in concentration at the site. This is in contradiction with the change in weather, which got increasingly drier and warmer up to 12 June. The field is a net source at nighttime only on 31 May. With an average emission of 0.5 mg NH$_3$ m$^{-2}$ day$^{-1}$ during the first 5 days, the grazing fluxes were an order of magnitude lower than at Easter Bush, while the last 5 days averaged to -2.5 mg NH$_3$ m$^{-2}$ day$^{-1}$. Although based on a short time series, this would suggest that an ungrazed field at this location would receive an NH$_3$ dry deposition input of the order of 7.5 kg NH$_3$ ha$^{-1}$ yr$^{-1}$.
1.2.3 **INTERCOMPARISON OF AMMONIA MEASUREMENT TECHNIQUES**

Ammonia is estimated to dominate N dry deposition in large parts of the UK, yet the automated measurement of ammonia concentrations and fluxes at ambient levels still provides a major challenge. Wet chemistry analysers like the AMANDA and MARGA instruments are labour intensive and therefore too costly for application in large networks. In the UK, the two MARGA instruments at Auchencorth and Harwell EMEP Supersites now provide hourly concentrations of NH$_3$. By contrast, the spatial pattern is derived from monthly measurements (by ALPHA diffusion and DELTA denuder sampler) from the UK Ammonia Monitoring Network (now UKEAP), which provides a good geographic picture, but limited information on temporal variability and thus on some of the processes controlling NH$_3$ concentrations. In addition, due to the costs involved, NH$_3$ flux measurements are limited to short-term intensive studies over selected surfaces and the database on parameters needed for process modelling of bi-directional NH$_3$ exchange is still incomplete.
Through collaboration with the European NitroEurope IP and a NERC grant, CEH was able to organize a major international inter-comparison campaign of real-time monitoring techniques for atmospheric ammonia and surface / atmosphere exchange fluxes at Easter Bush, which coincided with one of the AMANDA flux measurement periods reported above. Eleven instruments were operated over three weeks by groups from the UK, Canada, Finland and Hungary, with CEH leading the co-ordination and overall analysis. In order to test the instruments over a wide range of ambient concentrations the first half of the measurement period was made at ambient concentrations before the field was fertilized with urea to induce larger concentrations and fluxes.

**Table 1.2.** Summary of the characteristics of the instruments.

<table>
<thead>
<tr>
<th>Instrument</th>
<th>Technique</th>
<th>Manufacturer</th>
<th>Air flow rate [lpm]</th>
<th>Used time resolution / used time average [s]</th>
<th>precision [ppbv]</th>
<th>Range [ppbv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>RBD</td>
<td>Batch denuder / offline FIA</td>
<td>ECN (Keuken et al., 1988)</td>
<td>27</td>
<td>2400 / 3600</td>
<td>0.01</td>
<td>Unknown</td>
</tr>
<tr>
<td>AMANDA</td>
<td>Wet denuder / online FIA</td>
<td>ECN (Wyers et al., 1993)</td>
<td>28</td>
<td>450 / 450</td>
<td>0.02</td>
<td>0.02 - 500</td>
</tr>
<tr>
<td>AiRRmonia</td>
<td>Diffusion scrubber / online FIA</td>
<td>R&amp;R Mechatronics</td>
<td>1</td>
<td>60 / 60</td>
<td>0.05</td>
<td>0.04 - 500</td>
</tr>
<tr>
<td>DUAL-QCLAS</td>
<td>Quantum cascade laser absorption spectrometry</td>
<td>Aerodyne Research, Inc. (ARI) (Whitehead et al., 2008)</td>
<td>15</td>
<td>0.2 / 60</td>
<td>0.018</td>
<td>Unknown</td>
</tr>
<tr>
<td>c-QCLAS</td>
<td>Quantum cascade laser absorption spectrometry</td>
<td>Aerodyne Research, Inc. (ARI) (McManus et al., 2007)</td>
<td>8.9</td>
<td>1 / 60</td>
<td>0.05</td>
<td>Unknown</td>
</tr>
<tr>
<td>WaSul</td>
<td>Photo-acoustic spectroscopy</td>
<td>Hilase Ltd.</td>
<td>4</td>
<td>300 -1800/300 -1800</td>
<td>0.25</td>
<td>0.25 - 100000</td>
</tr>
<tr>
<td>Nitrolux-100</td>
<td>Photo-acoustic spectroscopy</td>
<td>Pranalytica Inc. (Cowen et al., 2004)</td>
<td>1.2 - 1.6</td>
<td>3 / 300</td>
<td>0.1</td>
<td>0.1 - 200</td>
</tr>
<tr>
<td>CRDS</td>
<td>Cavity ringdown spectroscopy</td>
<td>EnviroSense1000 Analyzer, Picarro (Berden et al., 2000)</td>
<td>1</td>
<td>3 / 300</td>
<td>0.07</td>
<td>0.07 - 25</td>
</tr>
<tr>
<td>CIMS</td>
<td>Chemical ion mass spectrometry</td>
<td>Georgia Institute of Technology CIMS team (Nowak et al., 2007)</td>
<td>19.5</td>
<td>1 / 60</td>
<td>0.94</td>
<td>Unknown</td>
</tr>
<tr>
<td>IMS</td>
<td>Ion mobility spectroscopy</td>
<td>Bruker Daltonics</td>
<td>0.4</td>
<td>4 / 60</td>
<td>Unknown</td>
<td>Variable</td>
</tr>
</tbody>
</table>
Figure 1.2g. Scatter plots of the various instruments against a reference (calculated as the median of the different instruments).

From the results and experience during the campaign the following conclusions can be drawn on the current availability of instrumentation for application for UK NH₃ monitoring:

- The length and quality of the inlet are a major limitation for the quality of the measurement, especially at low concentrations. Here the (almost inlet-less) wet-chemistry systems have an advantage. For eddy-covariance flux measurements a longer inlet is required as the sample needs to be taken near the anemometer, while the instrument has to be located well away from the anemometer so as not to disrupt the air flow. This compromises the data quality for absolute concentrations.

- Some instruments (Nitrolux-100, Picarro CRDS, Wasul) use an inlet filter, which needs to be replaced very regularly (daily) to avoid aerosol dynamics on the filter affecting the measurement. This implies much shorter servicing intervals than stated by some of the manufacturers (e.g. Pranalytica for the NitroLux-100).

- Some instruments (QCLAS, CIMS) require continuous (e.g. hourly) gas-phase calibration in the field, but then provide good results. The provision of an accurate gas-phase calibration source contributes to the challenge of operating these instruments. Although theoretically an absolute instrument, without calibration the QCLAS under-reads by typically 30 to 40%.
The IMS is only suited to very low concentrations (< 5 ppb) and conditions where no other compounds may interfere with this non-specific technique.

The AMANDA, AiRRmonia, WaSul and IMS provide the most reliable results at low concentrations (< 10 ppb).

With weekly service intervals, the AiRRmonia provides one of the best compromises between purchase price, running costs, robustness and performance. The WaSul technique looks promising for concentration measurements but is still at an early development stage.

For flux measurements the AMANDA instruments continues to provide the most sensitive approach. Gradient measurements with the WaSul and eddy-covariance measurements by QCLAS provide reliable fluxes only if fluxes are large (> 100 ng m\(^{-2}\) s\(^{-1}\)).

### 1.3 Integrated deposition monitoring at Auchencorth Moss by Time Averaged Gradient Technique

Integrated deposition monitoring using a low-cost flux measurement technique developed at CEH Edinburgh was installed at Auchencorth during the original Acid Deposition Processes project and continued throughout the duration of the extension. The aim of this activity is to derive annual dry deposition inputs to sensitive moorland vegetation, which are based on actual flux measurements (as compared with inferential modelling estimates) but cost-efficient to obtain. This excludes the use of real-time analysers, which are very labour intensive to maintain for these compounds, and thus does not provide high temporal resolution fluxes (like the AMANDA used in the previous Section) which would be required to study the processes controlling surface / atmosphere exchange.

The conditional time averaged gradient (Co-TAG) system applied here measures monthly fluxes of a range of inorganic trace gases and aerosol components of atmospheric importance. These are derived from monthly concentration gradients, which are averaged over all but very stable and very unstable atmospheric conditions, applying an average flux / gradient relationship for the sampling conditions. The gradient is measured with DELTA type denuder / filter-pack samplers, operated at 5 heights on an eight-metre scaffolding, which are turned off during the extreme stratifications. While this technique has been shown to provide results for NH\(_3\) and SO\(_2\) with little bias for the sample period, the challenge is the gap-filling of the periods where the system does not sample.

Table 1.3a summarises the concentrations measured with the TAG during the sampling period. Concentrations at Auchencorth Moss are relatively low for all compounds. The time series of the monthly concentrations (\(\chi\)), fluxes (\(F\chi\)) and deposition velocities (\(V_d = -F\chi/\chi\)) are shown in Fig. 1.3a for three of the most important compounds (NH\(_3\), HNO\(_3\) and NH\(_4\)\(^+\)). At the beginning of the sampling period, in 2004/05, there were problems with leaks in the sampling train after addition of the filter packs, which, with the then poorer analytical precision for the anion analysis, led to significant sampling loss. Since the second half of 2005 the instrument has been working well, given the challenges due to low concentrations at this site. Individual sampling points had to be removed from the time-series as they did not pass the quality assurance criteria for the analytical chemical analysis and / or on the gradient itself.
Fluxes of NH$_3$ were continuously downwards, except for one sampling point in June 2007, which would be consistent with enhanced stomatal compensation points during this warm period. By contrast, fluxes of HNO$_3$ and NH$_4^+$ (as of the other compounds not shown here) are more variable with emission and deposition fluxes. The HNO$_3$ measurements are more variable in quality, but, surprisingly, the measured deposition velocity of HNO$_3$ is consistently lower than that of NH$_3$ which contradicts the general notion that HNO$_3$ is deposited with a zero surface resistance, while NH$_3$ experiences cuticular and stomatal uptake resistances at the ground. Aerosol deposition rates to short vegetation (as presented by the moorland) are usually in the region 0.1 to 5 mm s$^{-1}$. Fluxes of NH$_4^+$ measured at Auchencorth are small (within +/- 10 ng m$^{-2}$ s$^{-1}$), which makes them extremely challenging to be quantified with the current methodology. There are many months during which NH$_4^+$ shows apparent emission or during which NH$_4^+$ is deposited at a rate which is unlikely. However, faster apparent deposition rates have recently been found for NH$_4^+$ and NO$_3^-$ over semi-natural vegetation, probably due to NH$_4$NO$_3$ evaporation near the ground. This effect would lead to both fast NH$_4^+$ deposition and apparent slow HNO$_3$ deposition (or even emission).
Figure 1.3a. Time-series of (a) concentrations, (b) fluxes and (c) deposition velocities of example compounds (NH₃, HNO₃ and NH₄⁺) measured with the TAG system.

Table 1.3b summarises the total annual dry deposition inputs of the different compounds as derived from the filtered TAG data. This table includes two alternative estimates: the first (average) estimates represents the average flux detected during the TAG sampling periods (i.e. excluding very stable and unstable conditions), which was upscaled to the entire year. This implies that during the extreme stratification, the average flux would need to be the same as during the near neutral conditions. This estimate is likely to represent an overestimate of the deposition as during highly stable conditions atmospheric resistances are large and dry deposition usually very limited, while highly unstable conditions often occur during the warmest part of the day, when stomatal compensation points are largest and most of the potential for emission may occur. The second (alternative) flux estimate was calculated assuming that the measured flux is also representative for very unstable conditions, but that the flux is negligible during very stable conditions. We believe that this is the more realistic estimate. Although the individual flux measurement for a single month may be uncertain, some of the dry deposition estimates look very robust. In particular, dry deposition estimates of NH₃ are very similar between years. By contrast, concentrations of the base cations (Na⁺, Ca²⁺ and Mg²⁺) are too small for the gradients to be determined with sufficient accuracy and the results are unlikely to be reliable. In general, blank variability was larger on the filters (for aerosol sampling) than on the denuders (for gas sampling). The chemical analytical technique also struggled with the low concentrations of the chloride and sulphate compounds.
Table 1.3b. Annual dry deposition budgets of the different compounds measured with the TAG flux system, comparing two estimates, based on the average measured during the sampling period and one (alternative) based on the flux being negligible during very stable conditions. Negative fluxes represent deposition.

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>SO₂⁻⁻S</td>
<td>0.54</td>
<td>0.45</td>
<td>-0.17</td>
<td>-0.15</td>
<td>-0.16</td>
<td>-0.15</td>
<td>-0.69</td>
<td>-0.65</td>
</tr>
<tr>
<td>SO₄²⁻⁻S</td>
<td>0.30</td>
<td>0.25</td>
<td>-1.26</td>
<td>-1.08</td>
<td>-0.26</td>
<td>-0.24</td>
<td>-0.04</td>
<td>-0.04</td>
</tr>
<tr>
<td>HNO₃⁻⁻N</td>
<td>-0.29</td>
<td>-0.25</td>
<td>-0.19</td>
<td>-0.17</td>
<td>-0.33</td>
<td>-0.32</td>
<td>-0.30</td>
<td>-0.28</td>
</tr>
<tr>
<td>NO₃⁻⁻N</td>
<td>-0.05</td>
<td>-0.04</td>
<td>-0.59</td>
<td>-0.51</td>
<td>0.14</td>
<td>0.13</td>
<td>-0.57</td>
<td>-0.54</td>
</tr>
<tr>
<td>HCl</td>
<td>-4.96</td>
<td>-4.20</td>
<td>-1.24</td>
<td>-1.06</td>
<td>-0.10</td>
<td>-0.10</td>
<td>-0.79</td>
<td>-0.74</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.43</td>
<td>0.36</td>
<td>-2.82</td>
<td>-2.41</td>
<td>1.70</td>
<td>1.62</td>
<td>-1.19</td>
<td>-1.12</td>
</tr>
<tr>
<td>NH₃-N</td>
<td>-4.17</td>
<td>-3.53</td>
<td>-4.20</td>
<td>-3.60</td>
<td>-3.93</td>
<td>-3.76</td>
<td>-4.21</td>
<td>-3.95</td>
</tr>
<tr>
<td>NH₄⁺-N</td>
<td>-0.35</td>
<td>-0.30</td>
<td>0.97</td>
<td>0.83</td>
<td>-0.18</td>
<td>-0.17</td>
<td>-0.35</td>
<td>-0.33</td>
</tr>
<tr>
<td>Na⁺</td>
<td>1.37</td>
<td>1.16</td>
<td>-6.34</td>
<td>-5.42</td>
<td>-0.20</td>
<td>-0.19</td>
<td>1.07</td>
<td>1.01</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>1.97</td>
<td>1.67</td>
<td>-0.96</td>
<td>-0.82</td>
<td>-0.40</td>
<td>-0.39</td>
<td>0.17</td>
<td>0.16</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>-0.52</td>
<td>-0.44</td>
<td>-1.32</td>
<td>-1.13</td>
<td>-0.89</td>
<td>-0.85</td>
<td>-1.10</td>
<td>-1.03</td>
</tr>
</tbody>
</table>

The measurements imply an average total dry deposition budget of 5.7 kg N yr⁻¹, which is dominated by NH₃ (83.0%), with minor contributions from HNO₃ (5.7%), aerosol NH₄⁺ (6.0%) and aerosol NO₃⁻ (5.4%). This compares with an average wet deposition input of 4 kg N yr⁻¹ at this site. In an earlier study, Flechard et al. (1998) derived a somewhat lower dry deposition input of 2.5 kg NH₃-N from one year of continuous AMANDA flux measurements. The lower deposition rate of HNO₃ as compared with the ones used in generating the CBED estimates (cf. Section 4) highlights the need to perform highly time-resolved HNO₃ flux measurements over UK vegetation.

### 1.4 Time-integrating relaxed eddy accumulation (TIREA)

The TAG approach has three limitations: firstly, it only measures the flux during near-neutral conditions, with assumptions required to fill in the remaining periods. Secondly, it has only been tested over short vegetation, while it is logistically difficult to deploy on tall towers, e.g. over forest. Thirdly, the denuder sampling is constrained to relatively low flow rates, limiting the detection limit. Higher flow rates would require very long denuder tubes which would be expensive, fragile and bulky. These restrictions sparked off the development of an alternative long-term averaging measurement system based on the relaxed eddy accumulation (REA) technique and high-flow filter packs, in collaboration with the European NitroEurope IP. In the REA approach, the flux is not derived from vertical concentration gradients, but two samplers are operated at the same height, one sampling air during up-draughts, the other during down-draughts. This sampling is controlled at 10 Hz, depending on the sign of the vertical wind components measured with an ultrasonic anemometer. The flux is calculated from the difference in the up- and down-draught concentrations,
combined with information on turbulence. In the time-averaging REA approach, three replicates were used each for up- and down-draughts.

The first dataset retrieved with the REA system showed that measurements are affected by large inter-variability of the replicate filters, resulting in large error bars. Initial leak-problems in the filter packs were solved, but this did not fully eliminate the scatter in the concentrations. The technical modifications (leakages and relays) led to an improvement in the data quality, but problems persist in the determination of the flow rates. Figure 1.4a shows the results from the Easter Bush campaign, where the REA system was operated in parallel to a TAG system and an AMANDA system. The results show a consistently large scatter: the method would have the benefit of flexibility in application above tall and short canopies, but at the present stage the scatter involved in the chemical analysis of the samples compromises the measurement of the fluxes. It was concluded that at the relatively high flow rates used here (to get sufficient aerosol loading) the accurate volume sampled by each filter pack is difficult to establish with low cost technology, especially because in the REA approach the flow switches on and off at a frequency of up to 10 Hz.
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Figure 1.4a. REA with high-flow filter-pack system results from the field campaign at Easter Bush in spring-summer 2007. Top to bottom: NH$_3$, NH$_4^+$, HNO$_3$ charts for concentration values, deposition velocities and fluxes.

1.5 Comparison between the two low-cost micrometeorological systems and the reference method on the field

The field campaign conducted at Easter Bush during spring-summer 2007 provided some comparison between the two low-cost systems with regards to the N compounds that were monitored. In Fig. 1.5a the linear regression between COTAG and REA shows good agreement between the fluxes monitored by the 2 systems ($r^2=0.83$). This is an encouraging result as the two methods are completely independent theoretically (relying on two different methods) and practically (different chemical analysis principles). The plot of the deposition velocities though reveals the real problem of the REA system, in that the scatter on the concentration measurements has strong repercussions on the deposition monitoring, and in most cases it is not possible to distinguish emission from deposition events.

Figure 1.5a. Linear regression between COTAG and REA systems on the measurements of fluxes of NH$_3$ and deposition velocities of NH$_3$ from the 2 systems. The values are weekly samples from the Easter Bush campaign (spring-summer 2007).
Figure 1.5b. Comparison between fluxes of NH$_3$ measured with TAG, REA, AMANDA at the Easter Bush field site in spring-summer 2007.

Figure 1.5b shows the summary plot of all NH$_3$ fluxes measured by the TAG, REA and AMANDA (reference method) systems. Again, the result is encouraging in that all the fluxes seem to follow the same behaviour, but when comparing the error bars it is evident that the REA system, although qualitatively detecting the same result, is not able to distinguish reliably between emission and deposition events because of the scatter on the points. By contrast, the TAG system presents an acceptable error level; however, it seems to be underestimating the fluxes when compared to the continuous gradient method (AMANDA): this result is in agreement with previous studies on the TAG system. The exclusion of the very stable and very unstable conditions (conditionality of the technique) causes a bias in the flux estimate, which can potentially be corrected by a constant factor dependent on the nature of the field site.

1.6 Measured concentrations of cloud chemistry at one representative UK upland site

The monitoring of orographic cloud and precipitation at high elevation sites in the UK is necessary to underpin the mapping of wet deposition throughout the country. The requirement arises because it is logistically very difficult (and expensive) to measure the wet deposition at high elevation locations where wet deposition is largest. The obvious problems of access are readily appreciated at mountain locations which receive 3000mm of precipitation annually at very remote locations. However, logistics are not the main problem because the enhanced precipitation is generated mainly through the seeder–feeder process in which pollutants present in orographic cloud are readily scavenged by the seeder rain (Fowler et al., 1988). The modelling and mapping of UK wet deposition requires estimates of the composition of the scavenged feeder cloud to show that the modelling procedures remain applicable in
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the longer term. In this report the data for the selected single location (Holme Moss) are presented. The collection of rain and cloud water samples has continued on a weekly basis without interruption. Supporting data on weather conditions including precipitation rate, precipitation type and duration along with standard meteorological measurements have also been gathered. The cloud concentration data are adjusted for the volume of rain water that would have been collected by the cloud gauge. Details were reported previously (SID4: March 2008).

The measured cloud and rainfall chemistry data over the entire monitoring period are summarised in Tables 1.6a and 1.6b. The data show consistently larger concentrations in cloud than rain, as expected, and a substantial long-term decline in non sea salt (nss) SO$_4^{2-}$ amounting to about 50% over the monitoring period. For the other ions there are also trends, with a decline in the marine ions Cl$^-$ and Na$^+$ of about 10% and a decline in NH$_4^+$ of approximately 30%, but with a much noisier data set. In particular, the concentrations of marine ions (especially Cl$^-$ and Na$^+$) show very large inter-year variability as they respond to the effects of the North Atlantic Oscillation on rainfall and wind speeds over the UK. The trends in concentrations of the two major anions, non-sea-salt (nss) SO$_4^{2-}$ and NO$_3^-$, are illustrated in Figure 1.6a. This trend is expressed as a ratio (nssSO$_4$:NO$_3$) and greatly reduces the inter-year variability in the signal.

The data show a pronounced decline in the nssSO$_4^{2-}$:NO$_3^-$ ratio driven mainly by the decline in nss SO$_4^{2-}$ concentrations. Table 1.6a shows concentrations of SO$_4^{2-}$ in rain declining from approx 35 $\mu$M in 1994 to 15 $\mu$M in 2008. Table 1.6b shows the concentrations in cloud declining from about 150 $\mu$M in 1994 to 70 $\mu$M in 2008, i.e. roughly declining by 50%, whereas NO$_3^-$ concentrations change little, ranging between 150 and 300 $\mu$M in cloud and 30 and 40 $\mu$M in rain, with no consistent time trend. The ratio of nssSO$_4^{2-}$:NO$_3^-$ in cloud concentration is less variable than the trends in concentration of the individual species, declining by approximately 50% between 1994 and 2008 (Figure 1.6b). In molar terms there is currently nearly three times as much nitrate as non-sea-salt sulphate in orographic cloud water and nearly twice as much NO$_3^-$ as nssSO$_4^{2-}$ in rainwater. This observation is consistent with the countrywide long term trends in nitrate and sulphate concentrations, which show small trends in NO$_3^-$ concentrations and large downwards trends in SO$_4^{2-}$ through the last 20 years.

Cloud composition data are important for the countrywide mapping of deposition to terrestrial surfaces, including the change in cloud composition with time. The wet deposition maps include an orographic enhancement based on observed differences between the composition of cloud water and rainwater. It is assumed that the scavenged cloud water concentrations exceed those in rainwater by a factor of two (Dore and Choularton, 1992). The data reported in Table 1.6a and 1.6b show larger concentrations in cloud than rain, as expected, but they also reveal differences between ions in the enhancement of cloud water concentrations. The ratio of concentrations in cloud and rain (reported March 2008) show values between 2 and 11 for the enhancement of cloud ion concentrations over rain. The general impression is of enhancement of cloud water ion concentrations for the key species (SO$_4^{2-}$, NO$_3^-$, NH$_4^+$) to be in the range 4 to 8. The ratio of concentrations in rain at the summit of Holme Moss to the reference, low level site (Wardlow Hay Cop) are shown in Figure 1.6c for the period 1994 to 2007. The rainfall enhancement shows great variability
between years, but averages a factor of two increases over the reference site for the 13 years. Concentrations of marine ions Cl\(^-\) and Na\(^+\) (and to a lesser extent Mg\(^{2+}\)) are always substantially larger at the hill top, by amounts ranging from 1.5 to 4.0 and there is some evidence that the enhancement has increased over the monitoring period, but the trend is obscured by the inter-year variability, with a mean value of 3.6 for Cl\(^-\) and 3.8 for Na\(^+\) over the 13 years. The enhancement of NO\(_3\)\(^-\) and nssSO\(_4\)\(^{2-}\) at Holme Moss is much smaller than for the marine ions, averaging 1.3.

Table 1.6a. Rainwater composition at Holme Moss 1994 to 2008 (annual volume weighted values).

<table>
<thead>
<tr>
<th>Original</th>
<th>Total</th>
<th>nss</th>
<th>Rain Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>NO(_3)(^-)</td>
<td>SO(_4)^{2-}</td>
<td>SO(_4)(^{2-})</td>
</tr>
<tr>
<td>1994 µM l(^{-1})</td>
<td>184</td>
<td>35.5</td>
<td>47.0</td>
</tr>
<tr>
<td>1995 µM l(^{-1})</td>
<td>177</td>
<td>33.0</td>
<td>45.3</td>
</tr>
<tr>
<td>1996 µM l(^{-1})</td>
<td>279</td>
<td>47.3</td>
<td>56.3</td>
</tr>
<tr>
<td>1997 µM l(^{-1})</td>
<td>215</td>
<td>44.0</td>
<td>48.9</td>
</tr>
<tr>
<td>1998 µM l(^{-1})</td>
<td>221</td>
<td>36.9</td>
<td>45.2</td>
</tr>
<tr>
<td>1999 µM l(^{-1})</td>
<td>218</td>
<td>43.0</td>
<td>43.2</td>
</tr>
<tr>
<td>2000 µM l(^{-1})</td>
<td>181</td>
<td>25.4</td>
<td>36.4</td>
</tr>
<tr>
<td>2001 µM l(^{-1})</td>
<td>170</td>
<td>23.4</td>
<td>36.2</td>
</tr>
<tr>
<td>2002 µM l(^{-1})</td>
<td>264</td>
<td>18.2</td>
<td>35.6</td>
</tr>
<tr>
<td>2003 µM l(^{-1})</td>
<td>214</td>
<td>19.6</td>
<td>31.0</td>
</tr>
<tr>
<td>2004 µM l(^{-1})</td>
<td>295</td>
<td>24.4</td>
<td>29.2</td>
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<tr>
<td>2005 µM l(^{-1})</td>
<td>200</td>
<td>35.5</td>
<td>30.0</td>
</tr>
<tr>
<td>2006 µM l(^{-1})</td>
<td>228</td>
<td>28.2</td>
<td>28.8</td>
</tr>
<tr>
<td>2007 µM l(^{-1})</td>
<td>290</td>
<td>24.3</td>
<td>29.5</td>
</tr>
<tr>
<td>2008 µM l(^{-1})</td>
<td>132</td>
<td>27.2</td>
<td>21.0</td>
</tr>
</tbody>
</table>

Table 1.6b. Cloud water composition at Holme Moss 1994 to 2008 (annual volume weighted values)

<table>
<thead>
<tr>
<th>total</th>
<th>total</th>
<th>nss</th>
<th>Na(^+)</th>
<th>NH(_4)^{+}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl(^-)</td>
<td>NO(_3)(^-)</td>
<td>SO(_4)^{2-}</td>
<td>SO(_4)(^{2-})</td>
<td></td>
</tr>
<tr>
<td>1994 µM l(^{-1})</td>
<td>1091</td>
<td>249</td>
<td>218</td>
<td>154</td>
</tr>
<tr>
<td>1995 µM l(^{-1})</td>
<td>1351</td>
<td>467</td>
<td>267</td>
<td>186</td>
</tr>
<tr>
<td>1996 µM l(^{-1})</td>
<td>898</td>
<td>274</td>
<td>202</td>
<td>150</td>
</tr>
<tr>
<td>1997 µM l(^{-1})</td>
<td>959</td>
<td>273</td>
<td>195</td>
<td>145</td>
</tr>
<tr>
<td>1998 µM l(^{-1})</td>
<td>1037</td>
<td>216</td>
<td>168</td>
<td>117</td>
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<tr>
<td>1999 µM l(^{-1})</td>
<td>720</td>
<td>198</td>
<td>139</td>
<td>93</td>
</tr>
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<td>2000 µM l(^{-1})</td>
<td>661</td>
<td>168</td>
<td>116</td>
<td>79</td>
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<tr>
<td>2001 µM l(^{-1})</td>
<td>709</td>
<td>199</td>
<td>144</td>
<td>106</td>
</tr>
<tr>
<td>2002 µM l(^{-1})</td>
<td>853</td>
<td>176</td>
<td>131</td>
<td>91</td>
</tr>
<tr>
<td>2003 µM l(^{-1})</td>
<td>628</td>
<td>156</td>
<td>100</td>
<td>66</td>
</tr>
<tr>
<td>2004 µM l(^{-1})</td>
<td>668</td>
<td>127</td>
<td>90</td>
<td>62</td>
</tr>
<tr>
<td>2005 µM l(^{-1})</td>
<td>736</td>
<td>248</td>
<td>123</td>
<td>86</td>
</tr>
<tr>
<td>2006 µM l(^{-1})</td>
<td>964</td>
<td>400</td>
<td>158</td>
<td>104</td>
</tr>
<tr>
<td>2007 µM l(^{-1})</td>
<td>927</td>
<td>259</td>
<td>133</td>
<td>79</td>
</tr>
<tr>
<td>2008 µM l(^{-1})</td>
<td>961</td>
<td>196</td>
<td>121</td>
<td>66</td>
</tr>
</tbody>
</table>
Figure 1.6a. The trend in nssSO$_4$ :NO$_3$ concentrations ($\mu$M:$\mu$M) in rain at Holme Moss between 1994 and 2008.

Figure 1.6b. Changes in the molar ratio of nssSO$_4$ :NO$_3$ in orographic cloud at Holme Moss between 1994 and 2008.

Figure 1.6c. The changes with time in the ratio of ionic concentrations Cl$^-$, nssSO$_4^{2-}$, NO$_3^-$, NH$_4^+$, Mg$^{2+}$, Na$^+$ and Ca$^{2+}$ in rain at the summit of Holme Moss to those in rain at the low level reference site (Wardlow Hay Cop).
The annual cloud deposition maps for 2005 (Section 4) show the annual inputs of \( \text{nssSO}_4^{2-} \), \( \text{NO}_3^- \), \( \text{NH}_4^+ \) and \( \text{Cl}^- \) by cloud deposition (also known as occult deposition because it is not detected by conventional rain chemistry collectors). The patterns of deposition closely match the high ground and in particular land above 300m. However, as the maps are calculated from the product of the cloud frequency, wind speed and cloud composition, and both wind speed is larger and cloud base is lower in the west of the UK, the increases in cloud deposition with altitude are greater in the west generally than inland or in the east. The peak deposition values are not large for any of the anthropogenic ions, and are typically < 1kg S or N ha\(^{-1}\) annually, but are much larger for the marine derived \( \text{Cl}^- \) and \( \text{Na}^+ \) (up to 20 kg ha\(^{-1}\) y\(^{-1}\) ). These deposition values do not greatly influence the annual deposition totals, and are primarily of interest as possible drivers of change in the vegetation soils and freshwaters of upland Britain.

2. IMPROVED METHODS FOR MODELLING WET AND DRY DEPOSITION (OBJECTIVE B)

2.1 A Generalised Parameterisation to Predict Bi-directional Surface/Atmosphere Exchange of \( \text{NH}_3 \)

Plant / atmosphere exchange of atmospheric ammonia is governed by two main pathways: deposition to leaf surfaces and bi-directional exchange with the leaf apoplast through the stomata. In addition, \( \text{NH}_3 \) may be exchanged with the soil. A resistance model that combines these pathways of exchange was proposed by (Nemitz et al., 2001) (Fig. 2.1a). In order to apply this model at the UK scale, generalised parameterisations of the resistances (\( R_a \), \( R_b \), \( R_{ac} \), \( R_{bg} \), \( R_s \) and \( R_w \)) as well as emission potential (\( \chi_s \) and \( \chi_g \)) are required. The atmospheric resistances (\( R_a \) and \( R_b \)) are also needed to describe the exchange of other compounds and can be derived from standard meteorological parameters. They are readily available in most chemical transport models (CTMs). Similarly, \( R_s \) also governs the exchange of water, \( \text{CO}_2 \) and \( \text{O}_3 \) and has been well researched and tabulated.

In the UK, the exchange with the soil becomes important mainly after fertilisation. Since fertiliser emissions are explicitly described in the UK models (including FRAME), these are not mechanistically modelled within this framework as this would lead to double-counting. Thus, the in-canopy resistances (\( R_{ac} + R_{bg} \)) are here set to infinity to switch off this pathway. This pathway may also be important for barren land and in highly senescent plant canopies where leaf litter on the soil surface contributes to emissions, but so far litter emissions are insufficiently understood for inclusion into this modelling framework. By contrast, for semi-natural vegetation and agricultural vegetation during the growth stage, any soil emissions are thought to be recaptured by the overlying canopy. This is different in drier desert climates.

Hence, the key parameters that are unique to \( \text{NH}_3 \) are the stomatal compensation point (\( \chi_s \)) and the cuticular resistance (\( R_w \)) and our work focuses on deriving generalised parameterisations for these compounds. In this task we work closely with EMEP/MSC-W to ensure that the parameterisations developed for the UK can be extended to the European scale and form a UK contribution to the further development of the EMEP model.
Figure 2.1a. Resistance diagram of the two-layer canopy compensation point model to describe bi-directional surface / atmosphere exchange of ammonia.

The stomatal compensation point
The comparative magnitude of the stomatal compensation point (χ_s) compared with the average ammonia concentration in the canopy (χ_c) determines whether the stomata emit ammonia (χ_s > χ_c) or take up ammonia (χ_s < χ_c). It represents the gas phase concentration in equilibrium with the [NH₄⁺] liquid concentration in the leaf apoplast (the liquid inside the leaves, between the cells, which is in direct contact with the atmosphere through the stomata). This equilibrium is given by the combined solubility and Henry equilibrium, which is a function of both, temperature (T) and pH (i.e. [H⁺] concentration):

\[
\chi_s = \frac{161500}{T} \exp(-10.378 \frac{T}{T^2}) \frac{[\text{NH}_4^+]}{[\text{H}^+]}; \quad \Gamma_s = \frac{[\text{NH}_4^+]}{[\text{H}^+]}
\]

The ratio of apoplastic concentrations of [NH₄⁺] and [H⁺] may be substituted by a dimensionless emission potential (Γ_s), limiting the number of required parameterisations.

Γ_s of unfertilised vegetation
Plant-physiological laboratory work using plants under controlled growth conditions has shown that apoplastic [NH₄⁺] is closely linked to the magnitude of the N supply to the plant. In addition, there is evidence that in areas of high atmospheric N deposition (e.g. The Netherlands), semi-natural vegetation often acts as a significant source of NH₃, when ambient levels drop. Thus it is likely that, for unfertilised vegetation, Γ_s depends on atmospheric N deposition, although it is also known to vary between plant species on the same plot and with growth stage. Table 2.1 lists values of Γ_s reported or derived from the literature, together with estimates of atmospheric N deposition. As demonstrated in Fig. 2.1b, there is a strong relationship between the two parameters. However, the variability at the low end (N_{dep} < 10 kg N ha⁻¹ yr⁻¹) still requires some
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explanation as the current uncertainty of a factor of 4 will have a significant influence on concentrations and life-time of NH₃ in very remote areas.

**Table 2.1.** Summary of values of $\Gamma_s$ derived from micrometeorological flux measurements, together with estimates of the average annual N deposition at the study sites.

<table>
<thead>
<tr>
<th>Geographical Region</th>
<th>Vegetation</th>
<th>$\Gamma_s$</th>
<th>N dep [kg ha(^{-1}) yr(^{-1})]</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Forests</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Belgium</td>
<td>Mixed Coniferous</td>
<td>3300</td>
<td>35</td>
<td>Neirynck and Ceulemans, 2008</td>
</tr>
<tr>
<td>N. Carolina</td>
<td>Loblolly pine</td>
<td>1300</td>
<td>14</td>
<td>Nemitz et al. (unpub.)</td>
</tr>
<tr>
<td>Colorado</td>
<td>Mixed Forest</td>
<td>132</td>
<td></td>
<td>Langord &amp; Fehsenfeld, 1992</td>
</tr>
<tr>
<td>Netherlands</td>
<td>Douglas fir / mixed</td>
<td>8500</td>
<td>42</td>
<td>Wyers &amp; Eriman, 1998</td>
</tr>
<tr>
<td><strong>Semi-natural grassland / moorland</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Colorado</td>
<td>Alpine Tundra</td>
<td>16</td>
<td>6.3</td>
<td>Rattray and Sievering, 2001</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>Heathland</td>
<td>2800</td>
<td></td>
<td>Erisman et al., 1994</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>Heathland</td>
<td>1200</td>
<td>26</td>
<td>Nemitz et al., 2004</td>
</tr>
<tr>
<td>The Netherlands</td>
<td>Unfertil. grassland</td>
<td>2200</td>
<td>30</td>
<td>Kruit et al., 2006</td>
</tr>
<tr>
<td>Hungary</td>
<td>Semi-nat. grassland</td>
<td>200</td>
<td>9.2</td>
<td>Horvath et al., 2005</td>
</tr>
<tr>
<td>Scotland</td>
<td>Upland moorland</td>
<td>50-130</td>
<td>6</td>
<td>Milford et al., 2001</td>
</tr>
<tr>
<td>Scotland</td>
<td>Lowland moorland</td>
<td>132</td>
<td>8</td>
<td>Flechard and Fowler, 1998</td>
</tr>
</tbody>
</table>

**Figure 2.1b.** Relationship between $\Gamma_s$ and annual N deposition of the data of Table 2.1, combining data from forests and grasslands/moorlands.

However, the relationship: $\Gamma_s = 115.2 + 0.0167 \times N_{\text{dep}}^{3.49}$

where $N_{\text{dep}}$ is the total atmospheric nitrogen deposition in kg N ha\(^{-1}\) yr\(^{-1}\), is recommended as a first predictor of $\Gamma_s$ for semi-natural vegetation. This approach adds some circularity into the modelling of NH₃ exchange, as NH₃ dry deposition is
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needed to predict $\Gamma_s$ and $\Gamma_s$ is needed to predict NH$_3$ dry deposition. Workarounds include (a) spinning up the model with a simpler dry deposition scheme or (b) basing the estimate of $N_{dep}$ on the results from the previous model year. Work is continuing to add laboratory data to the relationship of Figure 2.1b. This requires relating e.g. N content of growth solutions into deposition estimates.

$\Gamma_s$ of agricultural vegetation
For fertilised, agricultural vegetation, the N status of the plants is dominated by short term response to agricultural management (fertiliser events, cuts, grazing) rather than atmospheric inputs. Work is continuing to compile seasonal profiles of $\Gamma_s$ in relation to common agricultural practice for the major types of agricultural land-use types represented in the UK CTMs (FRAME, EMEP4UK).

The cuticular resistance
The cuticular resistance ($R_w$) describes the ability of the leaf surfaces to absorb and store NH$_3$. This ability depends on the amount of water stored on the leaf cuticle, which can be in the form of invisible microscopic water layers at relative humidity ($RH) < 100\%$ or in visible water after rain or dew fall. In addition, the ability depends on the amount of NH$_3$ these leaves are exposed to and is self-limiting, as well as on the presence of other, neutralising compounds, such as atmospheric acids and SO$_2$.

Various site-specific relationships of $R_w$ vs. $RH$ have been derived from micrometeorological flux measurements. Figure 2.1c summarises the parameterisations reported in the literature.

![Figure 2.1c. Compilation of parameterisations of $R_w$ during various field studies.](image)

Although there is a large range of values and shapes, there are commonalities which are being explored to derive a generalised parameterisation. At high $RH$, $R_w$ increases from semi-natural sites subject to low NH$_3$ concentrations (green colours) to Dutch and Belgian semi-natural sites subject to high NH$_3$ concentrations (blue colours) and
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further to fertilised agricultural sites (red and yellow colours), which emit NH₃ resulting in larger concentrations near the ground and faster saturation of the leaf water layers. Thus, $R_w$ increases as NH₃ increases in absolute terms, or in relation to SO₂ as demonstrated in Fig. 2.1d.

![Figure 2.1d](image)

**Figure 2.1d.** The cuticular resistance ($R_w$) evaluated at RH = 95% in relation to estimated average annual molar ratio of SO₂/NH₃ at different measurement sites.

The steepness of the relationship of $R_w$ vs. $RH$ is likely to be affected by the degree of hygroscopicity of the plant surfaces and may thus differ between plant species. In addition, the aerosol burden will have an impact on the amount of leaf water at $RH$ in the region of 45 to 95%, where deposited aerosol deliquesces. Work is ongoing to combine these effects into operational equations.

### 2.2 New parameters from UK measurements

The new NH₃ flux measurements made as part of this project were designed to derive additional model parameters for UK vegetation. One approach to derive $\Gamma_s$ from micrometeorological flux measurements is to identify the concentrations at those moments where the flux changes sign (from emission to deposition or *vice versa*) in dry conditions (e.g. $RH < 70\%$) and to investigate their dependence on temperature. For zero fluxes and high $R_w$, $\chi_s$ approaches $\chi_a$. Figure 2.2a shows this analysis for the flux measurements at Keenley, where the symbols are coloured by time. Also shown are the temperature response curves for three values of $\Gamma_s$, based on the known temperature dependence of the Henry and solubility equilibria. For comparison, Figure 2.2b shows the meteorological parameters during this measurement period. At the beginning of the measurement period, the field was subject to grazing at a stocking density of 6.5 sheep & lambs ha$^{-1}$. On 2 June 2008 the sheep were removed from the field in accordance with the guidelines for the management of this type of calcareous upland meadow. There seems to be a general decrease in $\Gamma_s$ from a value of around 2000 during grazing to a value of around 100 at the end of the measurement period. The exception is a cluster of points on the morning of 13 June (light blue), which appear to fall onto the $\Gamma_s = 2000$ line. This may be linked to cuticular desorption adding to the flux or NW wind direction during this period, with more limited fetch conditions.
An application of the compensation point model to the flux measurements at Keenley is shown in Fig. 2.2c. The model is based on the single-layer model with in-canopy resistance $R_{ac}$ set to infinity. The model was run with the following parameterisations for the surface resistances:

$$R_s = \min(5000, 40 \times (1 + 60 \text{ W m}^{-2}/S\ell) \text{ s m}^{-1}$$

$$R_w = 20 \exp((100 - 40)/\text{RH}) \text{ s m}^{-1}$$

where $S\ell$ is solar radiation in W m$^{-2}$ and RH is relative humidity in %.

$\Gamma_s$ was set to 400 while the sheep were in the field and then assumed to decay exponentially during this period. These values are initially somewhat larger than suggested by Figure 2.2a above, but then come into the range of the measurements of $\Gamma_s$. The resulting model fit to the measured time-series is encouraging overall but shows some periods of discrepancy. The model fails to describe fully the dynamics of the first four days when the sheep were still in the field, particularly under-predicting the emission on 30 May which was characterised by foggy conditions, cool temperatures and low solar radiation. In addition, it overestimates emissions on 2, 5 and 7 June (particularly in the afternoon), while it underestimates emissions on 6 June. In general, the model tends to perform best during SW wind directions (see wind arrows in Fig. 2.2b), while other wind directions may be influenced by patch sources and more limited (but theoretically sufficient) fetch conditions. In this model parameterisation the net flux during daytime is the difference between much larger stomatal emission and cuticular recapture. It should be noted, that this stomatal emission in reality probably reflects a soil emission component which would need to be simulated in the two-layer model.
Figure 2.2b. Meteorological parameters during the NH$_3$ measurement at Keenley Fell.

Figure 2.2c. Comparison between measured and modelled net fluxes ($F_t$) at Keenley Fell, together with model prediction of component fluxes ($F_s$ and $F_w$). Also shown are the time-course of $\Gamma_s$ used to drive the model and the resulting stomatal compensation point ($\chi_s$) in comparison with the air concentration ($\chi_a(1m)$).
Nevertheless since no large night-time emission fluxes were observed, the simpler single-layer model is doing a reasonable job in reproducing the net flux. These measurements provide the first estimate of the effective $\Gamma$ for extensively managed upland grassland in the UK.

2.3 Modelling dry deposition of SO$_2$ and NH$_3$

In order to model trends in deposition of sulphur and nitrogen, it is necessary to represent accurately certain non-linear processes concerning atmospheric rates of chemical transformation as well as exchange between the atmosphere and the surface. One such process concerns the deposition of SO$_2$ to the surface. Measurements of the deposition velocity of SO$_2$ at Auchencorth Moss show a generally increasing trend as the acidity of the environment has declined due to reductions in SO$_2$ emissions during the last decade (Figure 1.1b). The change in deposition velocity is related to a change in the canopy resistance $R_c$, which is found to be empirically correlated to measurements of the ratio of SO$_2$:NH$_3$ concentrations (Figure 2.3a). A simple linear correlation was assumed in the FRAME model:

$$R_c = 50 \times (SO_2/NH_3)$$  \hspace{1cm} (2.3.1)

The deposition velocity of SO$_2$ was calculated according to the equation:

$$V_d(SO_2) = (R_a + R_b + R_c)^{-1}$$  \hspace{1cm} (2.3.2)

Where:

- $R_a$ is the ‘aerodynamic resistance’ due to turbulent diffusion of material to the roughness elements of the surface.
- $R_b$ is the ‘laminar boundary layer resistance’ which describes the transfer due to molecular diffusion through the quasi-laminar layer around the roughness elements of the surface.
- $R_c$ is the ‘surface resistance’ which describes the ability of the surface itself to capture airborne material and is dependent on the nature of the surface.

Figure 2.3b illustrates the frequency distribution across the UK of the SO$_2$:NH$_3$ concentration ratio by mass of the approximately 11000 5 km model grid cells. This illustrates the striking change in the chemical composition of the atmosphere during a 15 year period.

![Figure 2.3a: Illustration of the canopy resistance parameterisation used in FRAME for calculation of the deposition velocity of SO$_2$ and the measured correlation between canopy resistance and the ratio of SO$_2$ to NH$_3$ concentrations](image-url)
FRAME was applied to model the concentrations and deposition of sulphur and nitrogen compounds during the period 1990-2005. Further details of this are given in contract report CPEA34 “Modelling the Deposition and Concentration of Long Range Air Pollutants.”

The mass deposition budgets of UK wet deposition of nitrogen and sulphur modelled with FRAME for the years 1990-2005 are illustrated in figure 2.3c, and compared with data from CBED. The model employed constant meteorology (precipitation data and wind frequency data was averaged over the period 1990-2005). The model was generally able to capture successfully the trends in wet deposition obtained from CBED by measurement and interpolation. It is notable that wet deposition showed significantly smaller reductions than emissions during the corresponding time period, particularly for oxidised nitrogen. This was attributed principally to two factors. Firstly, whilst emissions from land sources in the UK during this period decreased significantly, emissions of NOx and SO2 from international shipping increased. Secondly, due to emissions reductions, the depletion of atmospheric oxidants became less of a controlling factor in determining the rate of conversion of pre-cursor gases to sulphate and nitrate aerosol (which make a major contribution to wet deposition). The CBED results show that due to inter-annual variations in meteorology (general circulation and annual precipitation), trends in wet deposition of oxidised and reduced nitrogen were difficult to detect. One of the advantages of atmospheric transport models is that they can be run either with constant meteorology or including annual variations in meteorology. Inclusion of annually variable meteorology is described in contract report CPEA34, including past and future trends in exceedance of critical loads for acid deposition and nitrogen deposition.

A comparison of the CBED and FRAME deposition maps of sulphur and oxidised and reduced nitrogen is illustrated in figure 2.3d. Wet deposition of NHx shows reasonable agreement both spatially and in magnitude for the two data sets. In part this reflects use of common approaches for annual precipitation data (generated from the UKMO monitoring network) and for orographic enhancement of wet deposition.
by the seeder-feeder effect. A similar agreement is found for wet deposition of sulphate and nitrate. Notable differences occur for sulphur dry deposition with FRAME generally giving higher deposition and showing evidence of hot spots near ports and power stations. Spatial differences also occur for dry deposition of oxidised nitrogen. CBED generally gives higher deposition due to the high contribution of nitric acid deposition. With FRAME, deposition is highest near to the major sources (major roads and urban areas) due to the contribution of deposition of NO₂. Preliminary results of wet deposition of NHₓ generated with the EMEP4UK model are illustrated in figure 2.3e for the year 2003 (notable for being a particularly dry year). The model shows similar spatial patterns to CBED and FRAME which suggests that the WRF meteorological model is able to represent orographic precipitation at a 5 km resolution.

**Figure 2.3c:** Mass wet deposition budgets modelled with FRAME and calculated with CBED as well as changes in pre-cursor gaseous emissions for the period 1990-2005.
Figure 2.3d(i): Comparison of annual wet deposition of NH₃ with CBED (left) and FRAME (right) for 2004-6 (kg N ha⁻¹)

Figure 2.3d(ii): Comparison of annual dry deposition of SO₂ with CBED (left) and FRAME (right) for 2004-6 (kg S ha⁻¹)
Figure 2.3d(iii): Comparison of annual dry deposition of NO\textsubscript{y} with CBED (left) and FRAME (right) for 2004-6 (kg S Ha\textsuperscript{-1})

Figure 2.3e: EMEP4UK annual NH\textsubscript{x} wet deposition for the year 2003 (mg N m\textsuperscript{2} yr\textsuperscript{-1})
3. **FLUX MEASUREMENTS OF AEROSOLS AND MODEL PARAMETERISATION FOR APPLICATION TO UK (OBJECTIVES C & I)**

In former project estimates, aerosols contribute in the region of 5 to 15% to the national deposition of N and S. Most of this deposition is estimated to occur to rough surfaces such as forests and well developed crops. Improved parameterisations of aerosol dry deposition velocities are needed to narrow down these uncertainties and also to improve predictions of models for air quality and climate change.

3.1 **Evaluation of aerosol deposition to UK forest**

Flux measurements were made over a UK oak forest (Alice Holt, Hampshire) in July / August 2005 as part of the earlier Acid Deposition Processes project. These measurements have now been fully analysed. Particle number flux measurements were made with a condensation particle counter (CPC), counting all particles in the size-range 5 nm to 1 μm, while flux measurements of individual aerosol chemical compounds in sub-micron aerosol were made with a novel flux system. This system, based on an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS) measures ammonium (NH₄⁺), nitrate (NO₃⁻), sulphate (SO₄²⁻) and organic aerosol mass (OM), which can be further divided into (primary) combustion derived hydrocarbon like organic aerosol (HOA) and (secondary) oxygenated organic aerosol (OOA), formed from the oxidation of biogenic and anthropogenic volatile organic compounds (VOCs). In addition to measuring surface / atmosphere exchange of these compounds, the instrument determines the aerosol size distributions. In agreement with other measurements in the UK and worldwide, the secondary aerosol components all peak in the accumulation mode, centred around 600 nm. By contrast, the HOA shows a much wider size distribution, with a significant contribution from a finer mode, centred around 200 nm, reflecting combustion aerosol (Fig. 3.1a).

![Figure 3.1a. Average particle size distribution for the Q-AMS measurement period (21st July – 18th August) in relation to the transmission curve of the inlets of the CPC and the Q-AMS.](image-url)
Figure 3.1b shows the time-traces of the concentrations of total particle number ($\chi_{\text{CPC}}$), ozone ($\chi_{\text{O}_3}$), aerosol components and selected VOCs (benzene & acetonitrile) in relation to meteorological parameters. Also shown is the split of total organic mass (OM) into HOA and OOA. Aerosol concentrations were moderate. Spikes in OM are accompanied by spikes in VOCs indicating pollution episodes, possibly from nearby fires. Some compounds (e.g. OOA and NO$_3^-$) showed a clear diurnal cycle with night-time maxima (Fig. 3.1c). There are probably two contributing factors: the lower boundary layer height during night and the shift of gas / aerosol phase equilibria of (semi-)volatile aerosol components towards the aerosol phase during cooler, more humid conditions.

Average diurnal cycles of the measured fluxes (Fig. 3.1d) show that, on average, fluxes of particle numbers, NO$_3^-$ and OOA were downwards (deposition). By contrast, for SO$_4^{2-}$ apparent upward fluxes were observed and HOA exchange was bidirectional. The small but consistent SO$_4^{2-}$ emission fluxes are surprising, but have previously been reported for other forest sites (e.g. Duke Forest, North Carolina, and Speulder Bos, The Netherlands). They may therefore indicate that there is a source of yet unidentified highly reactive sulphur containing aerosol precursor gases from the forest environment, which has been missed in former studies.
Figure 3.1c: Time series data of (from the top) wind speed (wspd), rainfall (blue sticks), wind direction (wdir), RH (blue dotted), T (red solid), $\chi_{O_3}$ (green dotted), $\chi_{CPC}$ (purple solid), chemically speciated Q-AMS concentrations, stacked OOA (pink) and HOA (grey), and PTR-MS time trace of benzene ($m/z$ 79, black dotted line) and acetonitrile ($m/z$ 42, purple solid line).
Figure 3.1d. Diurnal $\chi_i$ and $F_i$ of particle number and aerosol measure species, NO$_3^-$, SO$_4^{2-}$, OOA and HOA. Dotted lines are medians and solid are means. Shaded area indicates 5th-95th percentile range.

Figure 3.1e shows the time series of the deposition velocities ($V_d$) of the various aerosol components. With up to 50 mm s$^{-1}$, deposition velocities of NO$_3^-$ are surprising large, but well within the limits imposed by turbulence. The high values may indicate that there are sinks other than physical deposition, such as NH$_4$NO$_3$ evaporation near the warm forest canopy during daytime.
Figure 3.1e. Example time-series of the deposition velocities ($V_d$) of NO$_3^-$ (Top), HOA and OOA (Middle), and SO$_4^{2-}$ and CPC (Bottom).

Figure 3.1f shows the average values of $V_d$ for particle number, HOA and NO$_3^-$, binned for various values of friction velocity ($u_*$). All metrics show an increase in $V_d$ with $u_*$. The largest values of $V_d$ were observed for NO$_3^-$, for which evaporation sinks may contribute to the downward flux. The smallest values of $V_d$ were observed for total particle number fluxes. It is possible that upward moving components (such as SO$_4^{2-}$) affect these fluxes. More importantly, the particle number flux is dominated by very fine particles ($d_p < 100$ nm), for which removal mechanisms are known to be less efficient than for the accumulation mode which dominates deposition rates for HOA and NO$_3^-$. The data imply normalized deposition velocities ($V_d/u_*$) of 0.0052, 0.021 and 0.032 for numbers, HOA and NO$_3^-$, respectively. For comparison, former UK modelling of aerosol dry deposition to forest used values of 0.0198, 0.0221 and 0.0317 for NH$_4^+$, SO$_4^{2-}$ and NO$_3^-$, respectively, surprisingly close to the new parameterisations.
The measurements highlight that the effective deposition velocity of volatile compounds such as NH$_4$NO$_3$ may be much larger than that predicted based on physical deposition process alone. During the deposition process particles approach the surface, where day-time temperatures are larger and concentrations of NH$_3$ and HNO$_3$ are depleted due to dry deposition. Both effects favour NH$_4$NO$_3$ evaporation compared with higher heights. Thus, the evaporation of NH$_4$NO$_3$ into NH$_3$ and HNO$_3$ provides an additional sink which is included in flux measurements made well above the ground. Since NH$_3$ and HNO$_3$ deposit at much larger rates than particles, the particle-to-gas conversion enhances the deposition of N. This process is likely to be confined to warm daytime conditions and may partially be responsible for the enhancement in dry deposition rates observed in highly unstable conditions (large temperature gradients, long diffusive time scales). At the same time, this process greatly reduces the atmospheric lifetime (and transport distance) of NH$_4$NO$_3$ in the atmosphere. This would imply that the formation of NO$_3^-$ in the atmosphere is more efficient and dynamic that previously assumed.

### 3.2 New particle flux measurements over UK vegetation

The new particle flux measurements originally agreed under this contract (objective c) were dropped to free up funds to support the UK contribution to the EMEP Intensive Measurement Period September/October 2008 (objective i, see Section 3.3).
3.3. **Operate aerosol analyzers as part of the September/October 2008 EMEP ‘Intensive’ field campaign at Bush and Harwell**

This objective was added to the Acid Deposition Processes programme through a contract variation, to fund online measurements of aerosol composition and reactive gases at Auchencorth, Bush and Harwell during the EMEP Intensive Measurement Period September / October 2008. This work replaces the originally planned new aerosol flux measurements (Section 3.2). The contract variation only funded the measurements themselves, but not the full data analysis and interpretation. Therefore only preliminary data are presented here, which are not fully ratified at this stage and should be treated with caution. The following measurements were made in the UK during the EMEP intensive measurement period 2008:

- Ongoing measurements of aerosol composition, reactive gases, black carbon and aerosol mass at the EMEP supersite Auchencorth Moss (funded through the EMEP Supersite Project).
- Measurements of PM$_1$ aerosol composition by quadrupole-based aerosol mass spectrometer (Q-AMS) at the Bush EMEP site. For a combination of logistic and financial reasons, the instrument could not be operated at Auchencorth. However, the proximity of the two sites enables comparison of the longer-lived compounds (funded through this Project).
- PM$_{2.5}$ measurements of organic carbon at Bush (funded through a previous contract variation to the EMEP Supersite project).
- Measurements of PM$_1$ aerosol composition by time-of-flight mass spectrometer based aerosol mass spectrometer (HR-ToF-AMS) at the Harwell EMEP Supersite (funded through this Project).
- Measurements of TSP and PM$_{2.5}$ aerosol composition as well as reactive gases and aerosols by GRAEGOR at the Harwell EMEP Supersite (funded through this Project).

Figure 3.3a shows the preliminary time-series of aerosol composition at Bush (by Q-AMS) and Auchencorth (by MARGA). The PM$_{2.5}$ measurement represents organic carbon with a filter sampler (OC; carbon mass only), while the PM$_1$ measurements represents total organic mass measured with the Q-AMS (i.e. including O, H and N). Figure 3.3b shows the time series of the inorganic gas concentrations measured at Auchencorth with the MARGA system. Preliminary results from the measurements at Harwell are shown in Figures 3.3c and 3.3d for the aerosol and gas-phase measurements, respectively. The full data analysis will be carried out as part of the EMEP Supersite contract extension.
Figure 3.3a. Aerosol composition of PM$_{10}$ (bold coloured line), PM$_{2.5}$ (thin coloured line) and NR PM$_{1}$ (black line) measured at Bush (PM$_{1}$) and Auchencorth (PM$_{2.5}$ & PM$_{10}$) during the EMEP intensive measurement period September / October 2008. Org represents Q-AMS organic carbon PM$_{1}$ (green) and daily integrated organic carbon (C only) PM$_{2.5}$ at Bush.

Figure 3.3b. Time-series of inorganic gas concentrations measured with the MARGA system at the Auchencorth EMEP supersite during the Intensive Measurement Period Sep/Oct 2008.
Figure 3.3c. Aerosol composition of TSP (bold coloured lines), PM$_{2.5}$ (dotted line) and NR PM$_1$ (black line) measured at Harwell during the EMEP intensive measurement period September / October 2008.

Figure 3.3d. Time-series of inorganic gas concentrations measured with the GRAEGOR system at the Harwell EMEP supersite during the Intensive Measurement Period Sep/Oct 2008.
4. HIGH RESOLUTION MAPS OF WET, DRY AND CLOUD DEPOSITION (OBJECTIVE D)

The following maps show the wet and dry deposition of material to the UK on a 1 km x 1km grid, marking a major improvement in spatial resolution from the previous 5 km x 5 km grid. These maps are based on measured air concentrations of gases and particles, and an inferential model that depends on land-use at the sub-grid scale (i.e. the distribution of different land uses within a grid cell). As noted above, wet deposition is calculated from an interpolated concentration field derived from low-elevation measurements, and combined with high spatial resolution precipitation data from the Meteorological Office. The seeder-feeder enhancement of deposition relies on the observed ratios of cloud and rain concentrations, which have not changed markedly over time, even though absolute concentrations have changed. Details of the methodology for producing these maps (Concentration Based Estimates of Deposition = CBED) have been described in earlier reports. The maps below are all for the year 2005 so that direct comparison can be made between wet and dry deposition. Only deposition maps for the major ions are shown, but maps are available also for sodium, magnesium, calcium (total and non-marine) and total sulphate deposition, and for concentrations in air and rain used to generate the deposition maps.

The process of generating the maps at 1 km using existing methods (i.e. using the software designed for 5 km mapping) proved to be very time-intensive, so only maps for 2005 have been generated (see below). There are also issues of data availability for meteorological information including precipitation depth at 1 km scale for 2006, and an incompatibility between 1 km and 5 km precipitation data for the UK which needs to be reconciled. Maps for 2004-2006 at 5 km resolution have been generated (not shown below) and data have been supplied to CEH Bangor for Critical Load Exceedance modelling in order to satisfy the UK sustainable development indicator no. 28 “Ecological impacts of air pollution”.

The maps follow a common format: wet deposition, aerosol dry deposition, cloud deposition, gaseous deposition, and total. The highest contour level (lilac) is shown for clarity above each map.
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**Non-marine sulphate**
- Wet (>7.9 kg S ha\(^{-1}\))
- Dry aerosol (>0.45 kg S ha\(^{-1}\))
- Cloud (>0.99 kg S ha\(^{-1}\))

**Sulphur dioxide**
- Dry (>7.2 kg N ha\(^{-1}\))

**Total non-marine oxidised sulphur**
- (>9.6 kg N ha\(^{-1}\))
Nitrate
Wet (>7.1 kg N ha\(^{-1}\))

Dry aerosol (>0.9 kg N ha\(^{-1}\))

Cloud (>0.9 kg N ha\(^{-1}\))

Nitrogen dioxide
Dry (>1.9 kg S ha\(^{-1}\))

Nitric acid
Dry (>1.5 kg N ha\(^{-1}\))

Total oxidised N
(>14 kg N ha\(^{-1}\))
Ammonium
Wet (>8.5 kg N ha\(^{-1}\))

Ammonia
Dry (>6.5 kg N ha\(^{-1}\))

Total reduced N
 (>13 kg N ha\(^{-1}\))

Total N (ox + red)
 (>25 kg N ha\(^{-1}\))

Dry aerosol (>0.9 kg N ha\(^{-1}\))

Cloud (>1.1 kg N ha\(^{-1}\))

Cloud droplet deposition of ammonium — 2004
5. SYNTHESIS (OBJECTIVES F-H)

The main synthesis and interpretation of the outputs from this project will be found in the forthcoming RoTAP report, which utilizes many of the findings on long-term trends and the deposition maps. We summarize here the main findings of the Acid Deposition Processes project, and set them in context from a policy aspect. One of the aims of this project was to provide Defra with a look ahead to emerging issues, whether from measurements or modelling approaches, that may affect how acid deposition (and eutrophication) is changing with time, and of how advances in scientific understanding and modelling capability impinge on the UK’s monitoring activities and attitudes to policy at both a national and international level.

One specific objective (h) was an improved website for dissemination of monitoring and mapping data, and this has been delivered at:

http://www.uk-pollutantdeposition.ceh.ac.uk/.

From this web site maps and data can be searched and downloaded. Examples of screenshots are shown in Figure 5.1-5.3 below. The EMEP data are only available to registered users, but the other network data and maps are available to everyone.
Figure 5.1: screenshot showing title page, with searchable (clickable) map of measuring sites, and near real-time data from the EMEP supersite.

Figure 5.2: screenshot showing nitrogen deposition map at 5km resolution. The underlying data can also be downloaded.
Figure 5.3: screenshot showing data for nitric acid, sulphur dioxide and hydrogen chloride at Moor House. The underlying data can also be downloaded.
6. SUMMARY OF RESULTS AND IMPLICATIONS FOR POLICY

Section 1.1:
- Air concentrations of SO\textsubscript{2} at Sutton Bonington are continuing to decrease slowly, approaching 1 \( \mu \text{g m}^{-3} \), and reflecting the decrease in SO\textsubscript{2} emissions in the UK.
- The deposition velocity for SO\textsubscript{2} at Auchencorth is continuing to increase slowly, possibly as a result of a decrease in the SO\textsubscript{2}:NH\textsubscript{3} ratio at the site.
- These results imply that dry deposition of SO\textsubscript{2} across the UK may not decrease in line with emissions, and that deposition models should take account of the relative air concentrations of SO\textsubscript{2} and NH\textsubscript{3}.

Section 1.2:
- Measurements of NH\textsubscript{3} fluxes above managed grassland showed the expected bi-directional behaviour in response to fertilizer application and grazing, and have provided additional data for modelling (see below).
- A field comparison of different instruments and techniques for measuring NH\textsubscript{3} fluxes confirmed that the AMANDA system was best for flux measurements at low concentrations, although other systems worked well at higher concentrations.

Sections 1.3-1.5:
- Conditional time-averaged gradient (COTAG) methods have provided long-term fluxes of trace gases. At Auchencorth Moss, it appears that deposition fluxes of HNO\textsubscript{3} are smaller than expected assuming perfect uptake at the surface; this requires further investigation at other sites.
- The Time-averaged Relaxed Accumulation (TIREA) method is not yet suitable for application because of large uncertainties in the measurements.
- Comparison of COTAG fluxes with those measured continuously show generally good agreement, but more work is required on reconciling data during periods unsuitable for COTAG measurements (too stable, or unstable conditions).
- If the flux of HNO\textsubscript{3} is shown at other sites to be smaller than expected, this has significant implications for the dry deposition of HNO\textsubscript{3} across the UK (overestimated), and for the UK nitrogen budget. It will also affect the outputs from deposition models which assume that HNO\textsubscript{3} fluxes are not controlled by surface conditions.

Section 1.6:
- Measurements of cloud and rain water show consistent decreases of non-marine sulphate concentrations over time, and of the non-marine sulphate:nitrate ratio.
- At Holme Moss, nitrate ion concentrations (in moles litre\textsuperscript{-1}) are now twice those of non-marine sulphate in rain, and three times greater in cloud.
- There is no time trend in the ratio of concentrations of ions in cloud and in rain for non-marine ions; an apparent increase in the ratio for marine ions is correlated with rainfall amounts.
- These results suggest that the assumptions made in modelling the seeder-feeder deposition process for wet deposition over the uplands of the UK do not need to change in response to the observed changes in concentrations over time, at least for the main acidifying and eutrophying ions.

Sections 2.1 and 2.2:
- An empirical correlation has been derived from a compilation of measurements made over a range of natural and semi-natural vegetation which permits the ratio
of leaf ammonium to leaf acidity (necessary for modelling bi-directional exchange of NH₃) to be predicted on the basis of total N deposition.

- Compilation of field data on surface resistance to NH₃ deposition has shown a wide range of behaviour, but some generalisations can be made, such as a strong inverse linear dependence of the surface resistance on the annual SO₂:NH₃ ratio.
- Results from field experiments are being used to improve the parameterisations of the models used to estimate NH₃ exchange. The complexity of the process means that simple models are unlikely to be able to portray the bi-directional nature of the flux, and the net exchange over a year, leading to uncertainty in NH₃ budgets (emission and deposition).
- The first ever NH₃ flux measurements over an extensively managed upland species-rich grassland (at particular risk from N deposition) have been used to evaluate current flux models using appropriate parameterisations, with success in separating the stomatal and surface fluxes (useful in understanding the underlying processes) while predicting the overall net flux.
- Modelling of the complexities of NH₃ exchange is improving as more measurement data under different conditions, and to different vegetation, are obtained. The underlying processes and model structure have been shown to work well, and sufficient data are becoming available so that generalisations can be made reliably across the landscape.
- The database on bi-directional ammonia exchange is approaching a state where it is worth attempting a first application of the bi-directional exchange scheme across Europe.
- There remains a complete lack of NH₃ dry deposition measurements to UK forests.

Section 2.3:

- In 1990 67% of surface air in the UK contained concentrations of SO₂ by mass which were higher than those of NH₃. By 2005 this figure had fallen to 11 %, with a dramatic shift towards air dominated by NH₃ concentrations.
- Modelling studies (using FRAME with constant average meteorology) replicated time trends in wet deposition of reduced N and oxidised S across the UK observed by measurements.
- Dry deposition estimates for SO₂ and oxidised N modelled by FRAME and derived from measurements differ significantly, partly because of differences in formulating dry deposition rates, and partly caused by differences in gas concentration estimates.
- The rapidly changing chemical climate in terms of SO₂:NH₃ ratios, and oxidant to emission ratios, may have large effects on transport distances and dry deposition that are not captured well by models, and for which basic measurement evidence is lacking.

Section 3:

- Small but consistent upward fluxes of sulphate aerosol above a forest suggest mechanisms for particle generation that are not understood.
- Large downward fluxes of NH₄NO₃ above forests are consistent with particle decomposition in addition to deposition. It is worth testing the use of empirical, enhanced deposition rates in atmospheric transport and deposition models.
- Deposition velocities for particle number, nitrate and hydrocarbon-like organic aerosol (HOA) to forest increased monotonically with friction velocity (u*).
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suggesting, at rates surprisingly close to those currently used for deposition modelling.

- High quality measurements of aerosol composition and inorganic aerosol precursor gas concentrations were made at Auchencorth/Bush and Harwell, as a UK contribution to the 3rd EMEP Intensive Measurement Period Sep/Oct 2008 and are awaiting full analysis and interpretation.

Section 4:

- Maps of pollutant concentration and deposition (wet, dry, cloud) have been produced on a 1km grid, increasing the spatial resolution by a factor of 25.
- The accuracy of the spatial representation relies on interpolation and extrapolation across the UK based on a limited number of measurement points; the maps may therefore convey the impression of greater precision than can be justified from the basis of the input data.
- The use of 1 km precipitation data, and high resolution land-use data, will have improved the relative distribution of deposition within the 5 km grid squares used previously, particularly for those substances for which deposition rates depend strongly on rainfall quantity (wet deposition) or land use (NH₃, HNO₃ dry deposition).

Section 5:

- Much of the synthesis derived from the results of this project has gone into the draft RoTAP (Review of Transboundary Air Pollution) report, which is currently under review.
- A web site has been developed (http://www.uk-pollutantdeposition.ceh.ac.uk/) for the dissemination of measurement data, deposition maps and detailed information on measurement sites, using interactive maps and charts.

REFERENCES

